



The Atlantic Ocean Acidification Test-bed, La Parguera, PR

D.K. Gledhill^{1,2}, Chris Langdon², Jorge Corredor³, Rik Wanninkhof², R. Jim Hendee², Wade R. McGillis⁴.

¹Rosenstiel School, University of Miami, 2600, Rickenbacker Causeway, Miami, FL 33149; ²Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, 4301 Rickenbacker Causeway, Miami, FL 33149;

³University of Puerto Rico, Mayaguez Campus (UPRM) Mayaguez Island La Parguera 908 Lajas 00667-0908 Puerto Rico; ⁴Lamont-Doherty Earth Observatory, Geochemistry, Columbia Uni., NY.

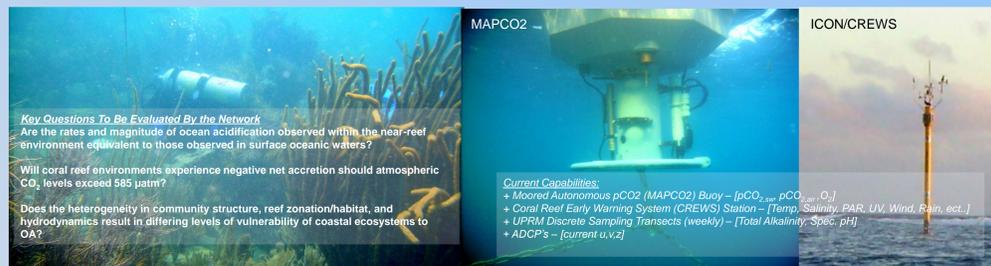


Lamont-Doherty Earth Observatory
COLUMBIA UNIVERSITY | EARTH INSTITUTE

INTRODUCTION

Changes in surface ocean chemistry in direct response to rising atmospheric carbon dioxide (CO₂) concentration may pose considerable challenges to a broad range of marine organisms in coming decades¹. Monitoring this ocean acidification (OA) at regional and local-scales is an important requirement towards improving our understanding of the potential long-term consequences. Coral reef ecosystems are of particular concern given the potential effects OA may have on coral growth rates²⁻⁴ and net community calcification⁵.

A satellite-based OA model is now routinely mapping the monthly distribution of surface ocean carbonate chemistry throughout the Greater Caribbean Region (NOAA CRW OAPS v0.4) and reveals considerable spatial and seasonal variability⁶. However, while such models offer an important regional geochemical context, they are applicable only to oceanic settings where coastal processes do not exhibit a significant influence. How OA is manifested within the shallow coastal waters where coral reef ecosystems reside is currently poorly characterized. Community-scale metabolic processes can impart an important control on near-reef carbonate chemistry. Constraining the near-reef variability in carbonate chemistry across diel, seasonal, and annual scales is a critical requirement to evaluating the potential geochemical thresholds of OA. The Atlantic OA Test-bed in the La Parguera Marine Reserve, Puerto Rico seeks to evaluate methodologies and technologies that could be employed to best monitor OA and its impacts within coral reef ecosystems.

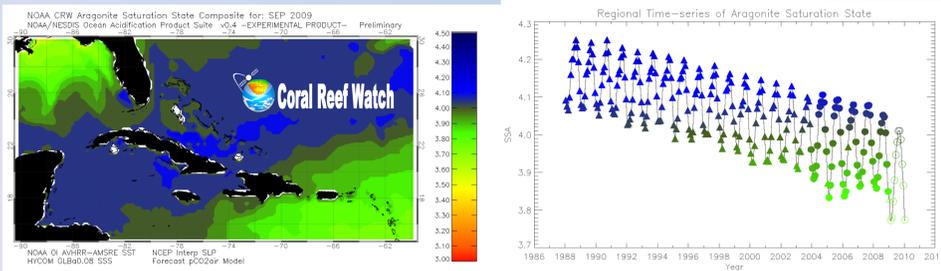


THE ATLANTIC OA TEST-BED

The NOAA Coral Reef Conservation Program has established an Atlantic OA Test-bed (AOAT) within the La Parguera Marine Reserve, Puerto Rico. The test-bed serves as an important prototype towards implementing a Coral Reef Ocean Acidification Monitoring Network. Since January 2009 the AOAT has provided sustained monitoring of near-reef air and sea pCO₂ and ancillary data coupled to weekly discrete geochemical transects across the Cayo Enrique foreereef.

La Parguera Marine Reserve

The natural reserve at La Parguera has been identified as a high-priority monitoring site for which on-going habitat characterizations are being conducted by UPRM. Significant reductions of live coral cover have been observed to occur within the reserve over the past several years with a notable decline following the 2005 Caribbean Bleaching Event. The decline of total live coral cover at the community level appears largely driven by mortality of *Montastraea annularis* which has served as the principle reef-building species in Puerto Rico. According to surveys conducted as part of the CCMA-BB's Caribbean Coral Reef Ecosystem Monitoring Project between 2001 – 2006, turf algae accounts for the highest mean percent cover, followed by macroalgae, gorgonians, hard coral and sponges⁷.



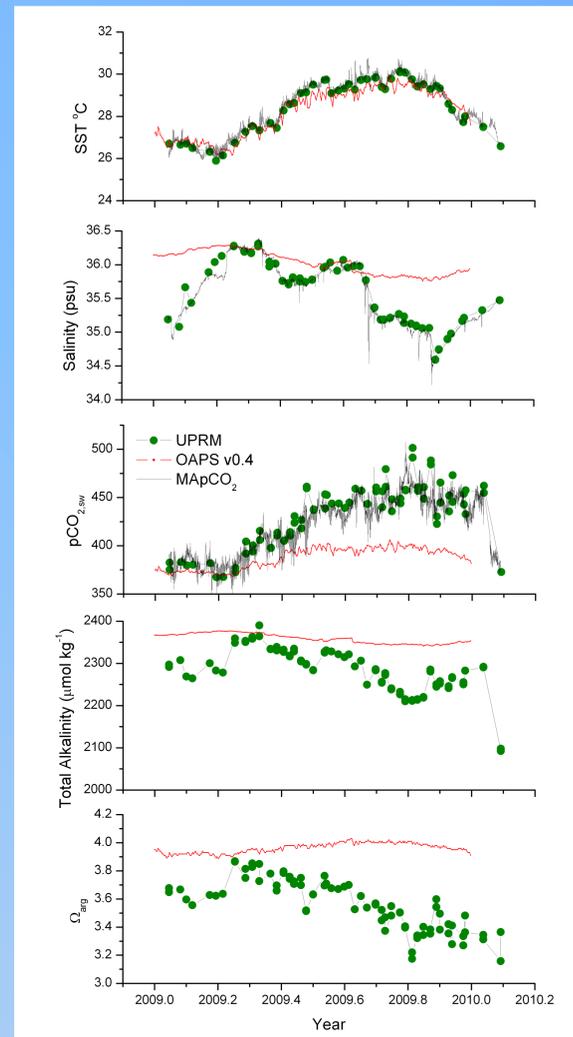
Ocean Acidification within the Greater Caribbean Region

The warm tropical oceanic waters of the South Atlantic and Caribbean exhibit some of the highest carbonate mineral saturation states of global oceans and are expected to remain supersaturated with respect to most carbonate mineral phases for the foreseeable future. However, due to the experimentally demonstrated positive relationship between the degree of supersaturation and calcification rates², OA could pose a threat to NOAA living marine resources within the region. Carbonate ion concentrations have already declined in tropical oceanic waters by more than 20% over the industrial period¹¹ with corresponding changes in carbonate mineral saturation. This degree of saturation is currently decreasing across the SER at a rate of about 3% per decade and exhibits considerable spatial and seasonal variability⁶.

Real Time MAPCO2 Data Available From www.pmel.noaa.gov/co2/coastal/LaParguera/data_La_Parguera_30d.htm

Coral Reef Early Warning System www.coral.noaa.gov/crews

OAPS v0.4 Available From www.coralreefwatch.noaa.gov/satellite/oa/



2009 CO₂-SYSTEM TIME-SERIES

Autonomous Measurements

The primary objective of the moored autonomous OA network will be to provide near continuous monitoring of a suite of chemical, physical, hydrodynamic, and meteorological measurements necessary to provide for the monitoring of community scale metabolic performance (net calcification, photosynthesis, respiration). The current test-bed provides a precursor of such a system whereby a Moored Autonomous pCO₂ (MAPCO2) buoy provides continuous 3 hourly measurements of both air and sea mole fraction CO₂ from the prevailing down-current end of Cayo Enrique Reef. The data are transmitted daily along with temperature, salinity and pressure and reviewed for QC by NOAA PMEL and posted to the web. These data are then routinely merged with oceanographic and meteorological data available from the nearby NOAA ICON/CREWS station.

Geochemical Transects

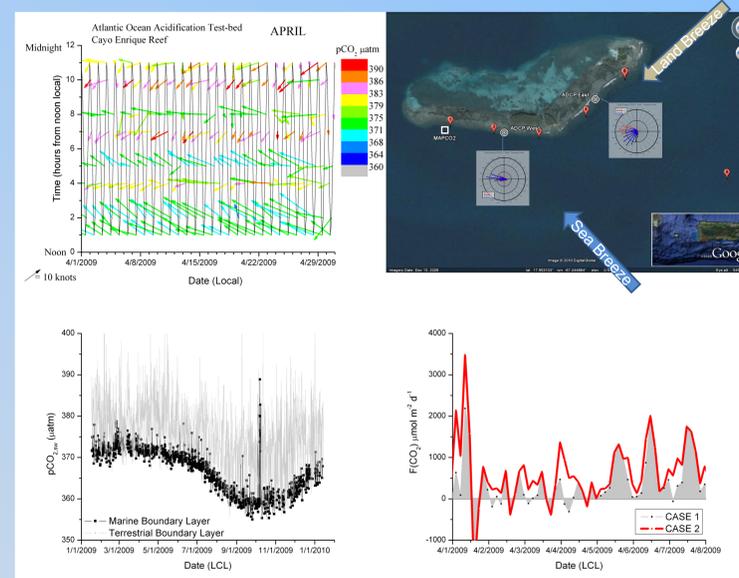
The autonomous observations are validated and supplemented on a weekly basis through a discrete sampling campaign conducted by UPRM. The campaign includes a CTD and water sample transect along the Cayo Enrique foreereef, at the MAPCO2, and 0.5 km up-current from the foreereef. Water samples are immediately processed at the nearby UPRM lab for total alkalinity (TA) and spectrophotometric pH.

pCO_{2,sw}

Discrete measurements of TA and pH obtained weekly by UPRM are coupled to solve for the carbonate acid system and aragonite saturation state using the CO2SYS program⁸ applying the K1 and K2 dissociation constants of Hansson and Mehrbach refit by Dickson and Millero, 1987 using total scale pH. The calculated pCO_{2,sw} (green circles) are in excellent agreement with the autonomous results obtained from the MAPCO2 buoy (grey line). In both cases, pCO_{2,sw} is observed to achieve values well in excess of 450 μatm throughout the summer and rapidly declines in January, 2010. These values are at least 50 μatm higher than that expected in the offshore Caribbean waters based on the OAPS v0.4 (red line). The 3 hourly pCO_{2,sw} measurements obtained at the MAPCO2 reveal considerable diurnal variability which is frequently underappreciated with regards to the effects of OA on coral reefs.

Aragonite Saturation State (Ω_{arg})

Aragonite saturation state (Ω_{arg}) describes the degree to which seawater is supersaturated with respect to the carbonate mineral aragonite of which most coral skeletons and reef structure are composed. Abiotic precipitation is thermodynamically favored at Ω_{arg} > 1 while dissolution occurs at Ω_{arg} < 1. Surprisingly, many laboratory experiments have found a functional relationship between coral calcification rates and Ω_{arg}. Beginning in early April, Ω_{arg} values at Cayo Enrique begin a systematic decline from near 4 to below 3.2. Such a decline is not apparent in the offshore OAPS v0.4 model. While the discrepancy between the OAPS and the test-bed is partly a reflection of coastal and reef processes, there is also reason to suspect based upon historical sampling at the offshore CaTS station (17° 36' N 67° 00' W; 17 miles from the shelf edge) that the HYCOM GLBa0.08 salinity fields used in producing the OAPS fail to capture the seasonal dynamics in the area and will need to be addressed as part of future OAPS development. At least part of the decline observed at the test-bed is related to the increasing pCO_{2,sw} observed at the site along with declining TA and salinity throughout much of the year. The attribution of the declining salinity is believed related to South American river inflow and local rainy season runoff.



SOME KEY FINDINGS SO FAR...

As a result of reef community metabolism, Cayo Enrique (like most other reefs⁹) serves as a net source of CO₂ to the atmosphere (ΔpCO₂ = 47 ± 34 μatm) albeit with a distinctive diel cycle where pCO_{2,sw} increases at night and subsequently declines throughout the day. This air-sea gradient works to drive off CO₂ from the water column according to $F_{CO_2} = k s p_{CO_2}$, where k is the gas transfer velocity derived from the nearby ICON/CREWS wind measurements and s is temp. & salinity dependent gas solubility¹⁰. However, within the coastal zone, this gradient can be strongly influenced by considerable variability in pCO_{2,air}. A key phenomenon not previously considered in the context of OA is the potential local effect that the terrestrial boundary layer pCO_{2,air} may have on the ability of a reef to off-gas CO₂ built up through metabolic activity. At Cayo Enrique a daily oscillation between the marine and terrestrial pCO_{2,air} boundary layer occurs. During periods when sea breeze conditions dominate (typically around noon time), the pCO_{2,air} is distinctly lower while at night when wind conditions become light and variable the terrestrial boundary layer prevails and elevates the local pCO_{2,air}. This terrestrial boundary layer will have a tendency to inhibit CO₂ flux from the water column (CASE 1) relative to what would occur in its absence (CASE 2). Whether such a phenomenon imparts a significant effect to local water chemistry is part of the on-going investigation at the AOAT.

1. Doney, S.C., V.J. Fabry, R.A. Feely, and J.A. Kleypas (2009). Ocean acidification: The other CO₂ problem. *Annu. Rev. Mar. Sci.*, 1, doi:10.1146/annurev.marine.010908.163834.169-192. 2. Langdon C. and M. J. Atkinson (2005). Effect of elevated pCO₂ on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *Journal of Geophysical Research*, 110(C09S07). 3. Gattuso J. P., M. Frankignoulle, I. Bourge, S. Romaine, and R. W. Buddemeier (1998). Effect of calcium carbonate saturation of seawater on coral calcification. *Global and Planetary Change*, 18, 37. 4. Marubini, F., H. Barnett, C. Langdon, and M. J. Atkinson (2001). Dependence of calcification on light and carbonate ion concentration for the hermatypic coral *Porites compressa*. *Mar. Ecol. Prog. Ser.*, 220, 153-162. 5. Silverman, J., B. Lazar, L. Cao, K. Caldeira, and J. Erez. Coral reefs may start dissolving when atmospheric CO₂ doubles. *Geophys. Res. Lett.*, 2009; DOI: 10.1029/2008GL036282. 6. Gledhill, D.K., Wanninkhof, R., Millero, F.J., Eakin, C.M., 2008. Ocean acidification of the Greater Caribbean Region. *J. Geophys. Res.* 113, C10031. 7. Jorge Garcia-Saiz, Richard Appeldoorn, Tim Battista, Laurie Bauer, Andy Bruckner, Chris Caldwell, Lisamaine Carrubba, Jorge Corredor, Ernesto Diaz, Craig Liljestrom, Graciela Garcia-Moliner, Edwin Hernandez-Delgado, Charles Menzies, Julio Morell, Anthony Paik, Jorge Sabater, Ernesto Weil, Ernest Williams and Stephanie Williams. 2008. The State of Coral Reef Ecosystems of Puerto Rico. pp. 75-116. In: J.E. Waddell and A.M. Clarke (eds.), *The State of Coral Reef Ecosystems of the United States and Pacific Freely Associated States: 2008*. NOAA Technical Memorandum NCS NCCOS 73. NOAA/NCCOS Center for Coastal Monitoring and Assessment's Biogeography Team. Silver Spring, MD. 569 pp. 8. Lewis, E., and D.W.R. Wallace. 1998. Program Developed for CO₂ System Calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. 9. Gattuso, J. P., M. Pichon, B. Delesalle, and M. Frankignoulle (1993). Community metabolism and air-sea CO₂ fluxes in a coral reef ecosystem (Morrea, French Polynesia). *Marine Ecology Progress Series*, 96, 259-267. 10. Wanninkhof R, Olsen A, Triñanes J (2007) Air-sea CO₂ fluxes in the Caribbean Sea from 2002-2004. *J Mar Syst* 66: 272-284. 11. Orr J. C., V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, R. M. Key, K. Lindsay, E. Maier-Reimer, R. Matear, P. Monfray, A. Mouchet, R. G. Najjar, G.-K. Plattner, K. B. Rodgers, C. L. Sabine, J. L. Sarmiento, R. Schlitzer, R. D. Slater, I. J. Totterdell, M.-F. Weirig, Y. Yamanaka, and A. Yool (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature*, 437, 681. 12. Jankulak, M., J. Hendee, and M. Shoemaker. 2008. The instrumental architecture of a Coral Reef Early Warning System (CREWS) station. *Proceedings of the 11th International Coral Reef Symposium*, Ft. Lauderdale, Florida, 7-11 July 2008 Session number 16.



dwright.gledhill@noaa.gov